



**Calhoun: The NPS Institutional Archive**  
**DSpace Repository**

---

Theses and Dissertations

1. Thesis and Dissertation Collection, all items

---

1970

The photochemical decomposition of 1, 3, 5,  
7-tetranitro-1, 3, 5, 7-tetrazacyclooctane (HMX).

Torbit, Jerry Bert

Monterey, California ; Naval Postgraduate School

---

<http://hdl.handle.net/10945/15126>

---

*Downloaded from NPS Archive: Calhoun*



Calhoun is the Naval Postgraduate School's public access digital repository for research materials and institutional publications created by the NPS community. Calhoun is named for Professor of Mathematics Guy K. Calhoun, NPS's first appointed -- and published -- scholarly author.

**Dudley Knox Library / Naval Postgraduate School**  
**411 Dyer Road / 1 University Circle**  
**Monterey, California USA 93943**

<http://www.nps.edu/library>

THE PHOTOCHEMICAL DECOMPOSITION OF 1,3,5,7-  
TETRANITRO-1,3,5,7-TETRAZACYCLOOCTANE (HMX)

Jerry Bert Torbit

LIBRARY  
NAVAL POSTGRADUATE SCHOOL  
MONTEREY, CALIF. 93940

# United States Naval Postgraduate School



## THESIS

THE PHOTOCHEMICAL DECOMPOSITION  
OF  
1,3,5,7-TETRANITRO-1,3,5,7-TETRAZACYCLOOCTANE  
(HMX)

by

Jerry Bert Torbit

April 1970

*This document has been approved for public re-  
lease and sale; its distribution is unlimited.*

T135311

LIBRARY  
NAVAL POSTGRADUATE SCHOOL  
MONTEREY, CALIF. 93940

The Photochemical Decomposition  
of  
1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX)

by

Jerry Bert Torbit  
Lieutenant Commander, United States Navy  
B. S., United States Naval Academy, 1962

Submitted in partial fulfillment of the  
requirements for the degree of

MASTER OF SCIENCE IN CHEMISTRY

from the

NAVAL POSTGRADUATE SCHOOL  
April 1970

Heil 1753  
C 1

ABSTRACT

This investigation was concerned with the photochemical decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX). Products from ultraviolet irradiation on both solid-state HMX and HMX-acetone solutions were obtained and identified.

On the basis of observed product variability with irradiation environment a new mechanism for the photochemical decomposition of HMX was postulated.

TABLE OF CONTENTS

I.	INTRODUCTION -----	9
II.	HISTORICAL -----	10
III.	EXPERIMENTAL -----	14
	A. PRELIMINARY INVESTIGATION -----	14
	B. EQUIPMENT UTILIZED -----	16
	1. Sample Preparation -----	16
	2. Sample Analysis -----	17
	C. THIN-LAYER CHROMATOGRAPHIC INVESTIGATION -----	17
	D. ULTRAVIOLET ABSORPTION INVESTIGATION -----	18
	E. INFRARED ABSORPTION INVESTIGATION -----	19
	1. Preparation of Solid Products -----	19
	2. Collection of Gaseous Products -----	20
	a. Irradiation of Solid HMX -----	20
	b. Irradiation of HMX-Acetone Solutions -----	20
	F. NUCLEAR MAGNETIC RESONANCE INVESTIGATION -----	21
	G. MASS SPECTROSCOPIC INVESTIGATION -----	21
	H. PHYSICAL PARAMETERS -----	22
	1. Mass Loss and Gas Evolution Determinations -----	22
	2. Melting Point Determinations -----	23
	3. Effects of Irradiation Upon Impact Sensitivity -----	23
IV.	RESULTS -----	24
V.	DISCUSSION -----	30
	BIBLIOGRAPHY -----	36
	INITIAL DISTRIBUTION LIST -----	40
	FORM DD 1473 -----	41





# LIST OF TABLES

	<u>PAGE</u>
I. Infrared Absorption Bands for Gaseous Products Obtained from Ultraviolet Irradiation of a Solution of HMX Dissolved in Acetone	26
II. Mass to Charge Ratios of Gaseous Products Obtained from Ultraviolet Irradiation of a Solution of HMX Dissolved in Acetone	27
III. Mass to Charge Ratios of Gaseous Products Obtained from Ultraviolet Irradiation of a Solution of HMX Dissolved in Acetone-d <sub>6</sub>	27
IV. Mass to Charge Ratios of Gaseous Products Obtained from Ultraviolet Irradiated and Non-Irradiated Reagent Grade Acetone	28
V. Mass to Charge Ratios of Gaseous Products Obtained from Ultraviolet Irradiation of Solid-State HMX at a Pressure of 0.001 Torr	28
VI. Mass to Charge Ratios of Gaseous Products Obtained from Ultraviolet Irradiation of Solid-State HMX Under an Atmosphere of Helium at a Pressure of 20 cm. of Mercury	29



## LIST OF DRAWINGS

### PAGE

1. Concentration of the N-NO<sub>2</sub> Chromophore  
as a Function of Irradiation Period 24
2. Proposed Mechanism for Photochemical  
Decomposition of HMX 34



## I. INTRODUCTION

Investigations concerning the reaction of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) when subjected to ultraviolet irradiation were first conducted in 1967. Other investigations have been concerned with the thermal decomposition and the effects of nuclear radiation upon HMX. The results of these investigations have been for the most part qualitative in nature, with no general agreement concerning either the reaction products or mechanism having been attained.

The purpose of the present investigation was to attempt to determine the reaction products resulting from ultra-violet irradiation of HMX and thereby to propose a mechanism for the reaction. To accomplish this HMX was irradiated both in the solid state and in acetone solution.

The variation of products with variations of irradiation environment led to the proposal of a new mechanism for photochemical decomposition of HMX.

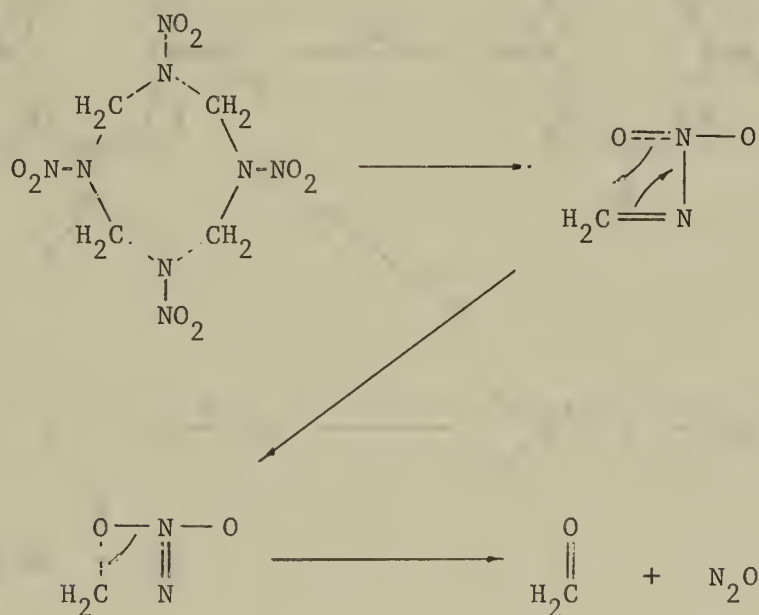
## II. HISTORICAL

The explosive compound 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX) was first isolated and identified in 1941 by Bachmann and Sheehan [1]. It was encountered as a by-product in the preparation of cyclo-trimethylenetrinitramine (RDX). At that time HMX was considered simply as an impurity in RDX, therefore scant attention was given it. They noted that the new compound was less soluble than RDX in hot aqueous nitric acid and that its melting point was higher than that of RDX, being somewhere above 256° C.

Subsequent crystallographic investigation [2] determined that HMX exists in four polymorphic forms, designated HMX I, HMX II, HMX III and HMX IV. HMX I was found to be the most stable polymorph at room temperature, the other polymorphs being stable at higher temperatures. The initial crystallographic work was refined in later years [3-5] by the use of x-ray diffraction techniques. Only one melting point was found (280° C) for all polymorphs, but solid-state transitions were observed at lower temperatures [5].

As knowledge accumulated concerning HMX its properties as an explosive were recognized as being in many ways superior to RDX. This realization prompted the generation of many new techniques for the manufacture of HMX in commercial quantities [6-15]. The chemistry of HMX was investigated during the same period [16,17] along with investigations into its absorption characteristics in the infrared [18] and the ultraviolet [19,20] spectra.

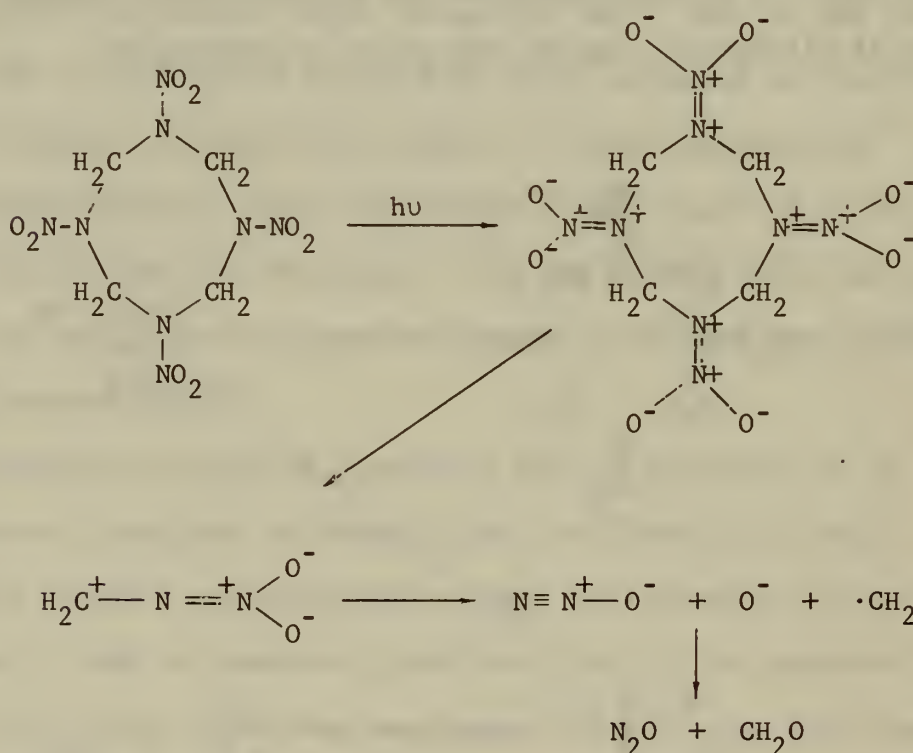
As with all explosives, considerations of gross stability or "shelf life" are important. Initial investigation into the thermal stability of HMX by Robertson [21] showed that upon heating above the melting point of  $280^{\circ}\text{C}$  HMX decomposed to give the following gaseous products, quantities given as moles product per mole HMX:  $\text{NO}(0.95)$ ,  $\text{N}_2\text{O}(1.51)$ ,  $\text{N}_2(1.16)$ ,  $\text{CO}(0.57)$  and  $\text{CO}_2(0.64)$ . Thermal decomposition studies by Maksinov [22], on the other hand, indicated that the major products were  $\text{NO}$  and  $\text{CH}_2\text{O}$ . The most recent work on thermal decomposition was conducted in 1967 [23]. This investigation determined the decomposition products to be as follows, quantities given as percentage total product:  $\text{N}_2\text{O}(40)$ ,  $\text{NO}(9.9)$ ,  $\text{N}_2(9.6)$ ,  $\text{HCN}(4.5)$ ,  $\text{CH}_2\text{O}(8.5)$ ,  $\text{CO}_2(8.5)$  and  $\text{CO}(4.1)$ . A proposed mechanism for decomposition, obtained through the use of nitrogen-15 tracers, was given as shown below:





Also in 1967, the first report appeared in the literature dealing with effects of ultraviolet irradiation upon HMX [24]. The investigators reported no products, but noted that irradiation caused the solid-state transitions to occur at reduced temperatures.

The most recent investigation into ultraviolet irradiation decomposition of HMX appeared in the literature during the course of this investigation [25]. The major products from ultraviolet irradiation of HMX I were reported to be  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$ . The following mechanism for decomposition was suggested:



Other investigators have studied the effects of nuclear radiation upon the  $\text{N-NO}_2$  chromophore [26,27]. Mollay and Prask [28] have investigated the effects of fission-fragment irradiation upon HMX. They concluded that the thermal initiation theory is inadequate to interpret the results of fission-fragment irradiation at elevated temperatures.

### III. EXPERIMENTAL

#### A. PRELIMINARY INVESTIGATION

The first phase of the investigation was to determine if HMX did, in fact, undergo a reaction when subjected to ultraviolet irradiation. To ascertain the presence or absence of photochemical reaction a colorless solution of 0.25 grams of HMX dissolved in 25 cc. of reagent grade acetone was placed in a fused silica reaction vessel and irradiated with a low pressure mercury vapor lamp for a period of four days. Upon completion of irradiation the solution has acquired a pale yellow color. After removing the acetone by means of a rotary evaporator operated at water-aspirator pressure, a light yellow solid remained indicating the possibility that a reaction had taken place. A strong, unidentified odor associated with the light yellow solid product was noted.

At this point the low pressure mercury vapor lamp was replaced with a PEK Labs 200 watt high-pressure mercury short-arc lamp. Another HMX-acetone solution was prepared as above and irradiated for 60 minutes. The results obtained previously were again observed. Pure reagent grade acetone was irradiated for 60 minutes. It remained clear throughout the irradiation. Sixty minute irradiations were conducted using ethyl acetate, cyclohexanone, cyclopentanone and gamma-butyrolactone as solvents. In each case the same color change and product odor was noted. It was further noted that when the solid product from the HMX-acetone solution irradiation was placed in an oven at 70<sup>0</sup> C for two hours the yellow color appeared to be enhanced, whereas non-irradiated HMX was not visibly affected under the same circumstances. Further irradiations

of HMX-acetone solutions demonstrated that as irradiation time increased the product progressed from a light yellow solid to darker yellow solid to a yellow-brown resinous substance.

On the basis of the results of the preliminary experiments it was considered probable that the HMX had undergone some sort of reaction. Since acetone boils at  $56.2^{\circ}\text{C}$  [29] it was considered unlikely that the reaction could be attributed solely to thermal effects.

The darkening of the yellow color of the solid product upon oven heating at  $70^{\circ}\text{C}$  indicated the possibility that there might have occurred an initial light-induced reaction which produced products more susceptible to thermal degradation than the non-irradiated HMX. To investigate this possibility a solution of 0.5 grams of HMX dissolved in 50 cc. of reagent grade acetone was placed in a pyrex flask connected to a water-cooled condenser and refluxed in a water bath while subjected to natural and fluorescent light. After a period of four hours the solution had acquired a pale yellow color. A fresh solution was prepared and refluxed as above, but in the absence of light. After a period of four hours the solution was found to have remained colorless. Removal of the acetone yielded a white solid identical in appearance to un-treated HMX.

In view of the paucity of information in the literature concerning this problem and the possible ramifications of such a reaction, it was considered worthwhile to explore the photochemistry of the HMX molecule. Determination of quantum yields, construction of energy manifolds and collection of rate data were recognized as being desirable, but due to the limited time available in which to conduct this investigation it



was decided to identify the products of the photochemical reaction and attempt thereby to formulate a possible mechanism for reaction.

## B. EQUIPMENT UTILIZED

### 1. Sample Preparation

All irradiations were conducted using a PEK Labs 200 watt high-pressure mercury short-arc lamp fitted with a parabolic reflector having an image distance of approximately eleven inches. Power was supplied to the lamp using a Oriel universal lamp power supply model number C-72-20. The spectral energy distribution of the lamp may be found on page 16 of PEK Labs catalog 21. The bands with energy in excess of 50 milliwatts per steradian-nanometer are located at 235-250, 305, 313, 330, 365, 405, 435, 545 and 575 nanometers.

Samples were irradiated in cylindrical fused silica reaction vessels permitting a path length of about 2 cm. through flattened irradiation surfaces having areas of about 12 cm<sup>2</sup>. One such vessel was attached to a water-cooled condenser and left open to the atmosphere. Another was fitted to allow connection to a vacuum manifold. A stopcock was located below the manifold connection to allow isolation of the reaction vessel. The reaction vessel was fitted with a side-arm containing a 10/30 standard taper connection to allow sample introduction without breaking the manifold vacuum. The side-arm also served as a connection for gas collection vessels, compressed gas tanks and a thermocouple gauge.

The vacuum system employed allowed collection of three gas samples from each irradiation. Temperature differentiation was attained by cooling the reaction vessel to the desired temperature and sampling the gases remaining uncondensed in the system. Vacuum

was obtained with the use of a single stage oil diffusion pump and with a mechanical vacuum pump connected so that it could also be used as a fore pump. Pressure measurements were made using a mercury manometer and a thermocouple gauge.

Gas samples for infrared absorption analysis were collected in a gas cell with KBr windows. The gas cell provided a path length of nine cm. and contained a volume of 113 cm<sup>3</sup>. Samples for mass spectrometric analysis were collected in pyrex bulbs attached through a capillary and stopcock to the vacuum manifold. Samples were removed by closing the stopcock and cutting the bulb from the system with a torch.

## 2. Sample Analysis

The following instruments were used for sample analysis:

Ultraviolet absorption	Beckman DB
Infrared absorption	Perkin-Elmer 621
Nuclear magnetic resonance	Hitachi Perkin-Elmer R-20A
Mass spectroscopy	CEC model A112

## C. THIN-LAYER CHROMATOGRAPHIC INVESTIGATION

Samples were prepared by irradiating solutions of 0.15 grams of HMX dissolved in 10 cc. of reagent grade acetone. Irradiations were conducted for various periods of time with the reaction vessel open to the atmosphere through a water-cooled condenser.

A series of 20 by 20 cm. glass plates were covered with a uniform 0.25 mm. layer of aluminum oxide and activated for 30 minutes at 105° C. Samples of non-irradiated and irradiated solutions were spotted on the plates and developed using a solution of 10% diethyl formamide in dichloroethane. Zinc dust and Griess' reagent were used as the indicator [30,31].

Preliminary investigations with various concentrations of non-irradiated HMX dissolved in reagent grade acetone showed that the amount of tailing afforded a visual means of determining the relative concentrations of nitramines present in the samples.

HMX-acetone solutions were prepared as above and irradiated for periods of 30, 60, 90 and 120 minutes. Several thin-layer chromatograms were prepared and analyzed with consistent results.

#### D. ULTRAVIOLET ABSORPTION INVESTIGATION

Samples were prepared by irradiating 25 cc. portions of a solution of 0.5 grams of HMX dissolved in 100 cc. of reagent grade acetone. Upon completion of irradiation the acetone was removed by means of a rotary evaporator. Since acetone does not transmit ultraviolet light of wavelengths shorter than 330  $m\mu$  [32] it was necessary to find a solvent transparent in the ultraviolet region of the spectrum. The major criteria for a solvent were considered to be the ability to dissolve HMX, adequate transmission of light of wavelengths greater than 210  $m\mu$  and absence of interfering reactions with either the non-irradiated HMX or the irradiation products. Acetonitrile, cyclohexane, heptane and hexane all transmit wavelengths in the ultraviolet region greater than 210  $m\mu$  [32]. Of these solvents, acetonitrile was experimentally determined to be the most satisfactory. As a result, spectrograde acetonitrile was used as the solvent in all ultraviolet absorption investigations.

Preliminary measurements showed that only one absorption peak at 227  $m\mu$  was present for both the non-irradiated and the irradiated HMX. The strength of this peak decreased with increased time of irradiation. By a trial and error method it was determined that to obtain the best



ultraviolet absorption spectrum the optimum concentration of HMX ([HMX]) in acetonitrile was  $4 \times 10^{-5}$  moles/liter (M). A solution of 0.5 grams of HMX dissolved in 100 cc. of reagent grade acetone was prepared. Ten cc. aliquots of this solution were taken for individual irradiation and analysis. One aliquot was not irradiated, while others were irradiated for periods of 10, 20, 30, 40 and 50 minutes. Upon completion of irradiation the acetone was removed by means of a rotary evaporator. Of each remaining solid 0.0030 grams were dissolved in sufficient acetonitrile to give 10 cc. of solution. One cc. of each such solution was then diluted with pure acetonitrile to 25 cc. This procedure resulted in the non-irradiated sample having an [HMX] of  $4 \times 10^{-5}$  M, the irradiated samples differing from this depending upon the amount of reaction having taken place.

#### E. INFRARED ABSORPTION INVESTIGATIONS

Samples for infrared absorption analysis were prepared by irradiating HMX both as a solid and as an HMX-acetone solution. Both solid and gaseous products were collected and analyzed.

##### 1. Preparation of Solid Products

Solid products were obtained by irradiating a solution of 0.5 grams of HMX dissolved in 25 cc. of reagent grade acetone in a fused silica reaction vessel open to the atmosphere. Solutions were irradiated for periods of time varying from fifteen seconds to four hours. Upon completion of irradiation the acetone was removed by means of a rotary evaporator. A portion of the remaining solid was mixed with sufficient KBr to yield a pellet approximately 0.5 mm. thick. Preparation and analysis was carried out for 26 such samples, including non-irradiated HMX and RDX. An additional infrared absorption spectrum



was obtained from a KBr pellet prepared using the solid product isolated as described in section III F.

## 2. Collection of Gaseous Products

### a. Irradiation of Solid HMX

HMX irradiations in the solid state were carried out in a fused silica reaction vessel attached to a vacuum manifold. 0.5 and 0.1 gram samples of HMX were deposited from a supersaturated acetone solution upon the inner surface of the reaction vessel. Deposition was carried out so as to place a thin even coating of HMX upon one flattened surface of the reaction vessel, the other surface remaining clean. The reaction vessel was placed on the vacuum line, evacuated to about  $10^{-3}$  Torr and allowed to de-gas for three days. The reaction vessel was positioned so that the light beam passed through the clean vessel surface before striking the HMX deposited on the opposite surface. Irradiations were then carried out with a stream of cool air directed over the reaction vessel, thus maintaining the HMX at or near room temperature in order to avoid thermal decomposition due to heating from the lamp. This procedure was employed for both the 0.5 and the 0.1 gram samples. It was found that satisfactory gas samples could be obtained by irradiating the 0.1 gram samples for 90 minutes. Samples for infrared analysis were taken at 20 and  $-78.5^{\circ}$  C. An additional irradiation of approximately 0.2 grams of solid-state HMX was carried out under an atmosphere of helium at a pressure of 20 cm. of mercury. A sample for infrared analysis was taken at  $20^{\circ}$  C.

### b. Irradiation of HMX-Acetone Solutions

A solution of 0.5 grams of HMX dissolved in 25 cc. of acetone was prepared and placed in the reaction vessel attached to the

vacuum manifold. The solution was cooled to  $-78.5^{\circ}\text{C}$  and the system was evacuated to  $10^{-3}$  Torr. The reaction vessel was then isolated from the manifold and irradiated for three hours. Upon completion of irradiation the sample solution was cooled to the desired temperature and the product gases allowed to expand into the system. Samples were taken at 20, -3,  $-78.5$  and  $-195.8^{\circ}\text{C}$ .

#### F. NUCLEAR MAGNETIC RESONANCE INVESTIGATION

Samples were prepared by dissolving 0.5 grams of HMX in 100 cc. of reagent grade acetone and irradiating 25 cc. portions of the solution for four hours. It was found that whereas HMX is insoluble in non-organic solvents the yellow-brown product was readily soluble in  $\text{H}_2\text{O}$ . Separation of products from remaining non-reacted HMX was accomplished by placing the residue in  $\text{H}_2\text{O}$  and filtering to remove the HMX. The  $\text{H}_2\text{O}$  was then removed by vacuum distillation and the resulting brown solid was weighed. Product solutions of approximately 15% by weight were prepared using  $\text{D}_2\text{O}$  as the solvent. The  $\text{D}_2\text{O}$  used contained one percent DDS (sodium 2,2-dimethyl-2-silapentane-5-sulfonate) which provided a reference at 0 ppm. [33].

#### G. MASS SPECTROSCOPIC INVESTIGATION

The procedures used to produce gas samples for mass spectroscopic analysis were identical to those used to produce gas samples for infrared absorption analysis. Product gases were allowed to expand into pyrex bulbs of 20 cc. capacity and removed by cutting the bulbs from the vacuum manifold with a torch. Samples were collected at temperatures of 20,  $-78.5$  and  $-195.8^{\circ}\text{C}$  from solid state HMX and HMX-acetone solution irradiations. One sample was collected from the

solid-state irradiation of HMX under an atmosphere of helium at a pressure of 20 cm. of mercury. Mass to charge (m/e) ratios from 12 to 110 were investigated.

## H. PHYSICAL PARAMETERS

### 1. Mass Loss and Gas Evolution Measurements

To obtain a measure of the mass loss of HMX upon irradiation a fused silica reaction vessel was first carefully cleaned and weighed. A sample of HMX weighing approximately 0.3 grams was then deposited from a supersaturated HMX-acetone solution upon one inside surface of the reaction vessel. After completely removing the acetone by oven drying for thirty minutes at 70<sup>0</sup> C the reaction vessel was again weighed, thus determining the precise mass of HMX deposited on the reaction surface to be 0.2784 grams. The sample was then irradiated while exposed to the atmosphere for two successive 90 minute periods. At the end of each irradiation period the vessel was weighed and the mass loss calculated.

To determine the relation between the mass lost and the quantity of gas evolved a 0.5036 gram sample of HMX was deposited on the inside surface of the reaction vessel fitted for connection to the vacuum manifold. The reaction vessel was placed on the vacuum manifold and the system was evacuated to 10<sup>-3</sup> Torr and allowed to de-gas for three days. The sample was then irradiated for 18 hours, the reaction vessel being cooled throughout this period by a stream of cool air. Throughout the period of irradiation the evolved gases were allowed to expand into the vacuum manifold, the volume of which had been previously determined. Upon completion of irradiation the pressure of the evolved gases was recorded.



The reaction vessel was removed from the manifold and the remaining solid was quantitatively transferred to a previously weighed flask by repeated washings with reagent grade acetone. The acetone was removed by means of a rotary evaporator and the flask was again weighed.

## 2. Melting Point Determinations

Melting points were obtained with a Fisher-Johns melting point apparatus and are presented herein as uncorrected values.

The melting point determined for non-irradiated HMX was within two degrees of a published value [5]. The melting point values obtained for irradiated samples varied widely, decreasing with increasing period of irradiation. The melting point of the pure product separated by  $H_2O$  solution and filtering was determined with good consistency.

## 3. Effects of Irradiation Upon Impact Sensitivity

A sample of irradiated HMX was prepared by dissolving 0.7 grams of HMX in 50 cc. of reagent grade acetone and irradiating the solution for 30 minutes in a fused silica reaction vessel open to the atmosphere. Upon completion of irradiation the acetone was removed by means of a rotary evaporator leaving a yellow solid.

Impact sensitivity determinations were conducted on both non-irradiated and irradiated HMX using the drop-test technique as outlined in Ref. 34. This method determines relative impact sensitivities of compounds on the basis of drop heights required for a given mass to attain a 50% probability of detonation upon impact with a static sample.

#### IV. RESULTS

Thin-layer chromatograms afforded visual evidence of a decreasing nitramine concentration with increasing period of irradiation. There was no indication of nitramines other than HMX present in the product.

The single absorption peak observed in the ultraviolet spectrum at 227 m $\mu$  was determined to be due to the N-NO<sub>2</sub> chromophore [19,20,35,36]. The decreasing strength of this band with increasing irradiation time showed the [N-NO<sub>2</sub>] to be a function of the period of irradiation.

Beer's law [32] was assumed to be valid in this instance and was accordingly used to calculate the absorptivity of the N-NO<sub>2</sub> chromophore from the known concentration of the non-irradiated sample. The value for absorptivity thus obtained was used to calculate the [N-NO<sub>2</sub>] for each of the irradiated samples. The results of those calculations are presented in Figure 1. The linear relationship shown in Figure 1 would indicate the presence of zero-order kinetics.

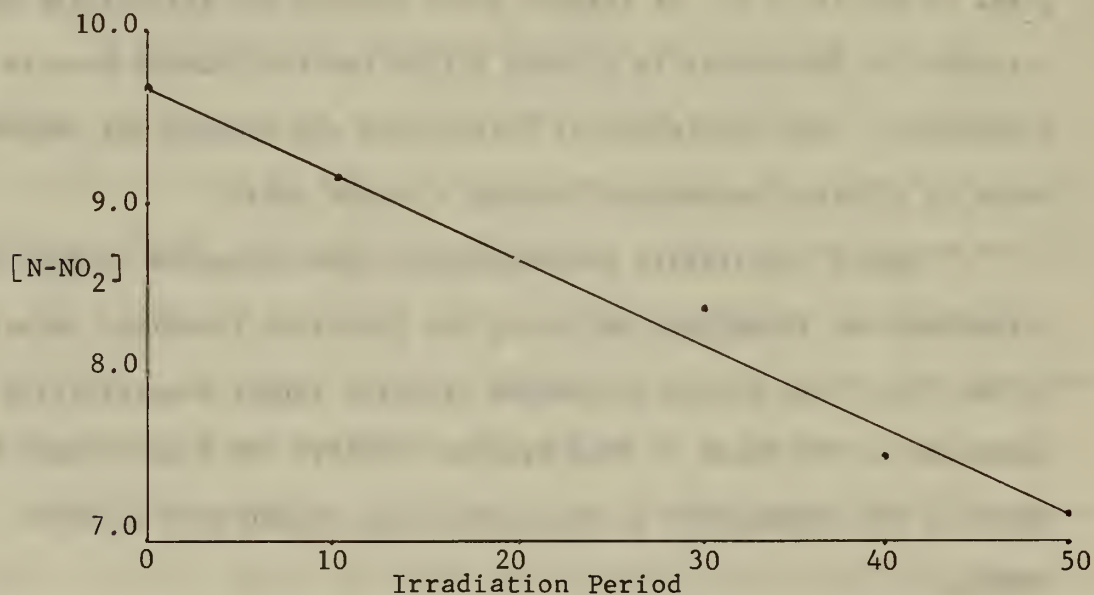


Figure 1. [N-NO<sub>2</sub>] (g/l × 10<sup>3</sup>) plotted as a function of irradiation period (minutes).

The HMX used in this investigation was ascertained to be in the form of the polymorph HMX I by comparison of infrared spectra obtained from non-irradiated HMX and published spectra for the polymorphs HMX I, HMX II and HMX III [5].

The only indication of change in molecular structure evidenced by the spectra of the solid products from irradiation of HMX-acetone solution was a marked decrease in the intensity of major absorption peaks at wave numbers 1275 and 1560. By the use of correlation charts provided by Beckman Instrument Corporation and Refs. 32 and 33 these peaks were identified as, respectively, single-bond and double-bond vibrations in the  $\text{N-NO}_2$  chromophore. The intensity of these peaks continued to decrease with increased periods of irradiation.

The infrared absorption spectrum of the isolated, water-soluble solid product showed broad, ill-defined bands around wavenumbers 1380 and 1670 and a very broad absorption in the area of wavenumber 3400.

The gaseous products obtained at 20° C from HMX-acetone solution irradiation yielded a spectrum showing strong (s), medium (m) and weak (w) absorption bands at wavenumbers 270 (s), 520 (m), 580 (m), 660 (w), 770 (w), 900 (w), 1080 (w), 1210 (s), 1270 (m), 1300 (s), 1360 (s), 1430 (w), 1730 (s), 2130 (w), 2210 (s), 2230 (s), 2330 (m), 2550 (w), 2800 (w), 2970 (m), 3020 (m), 3460 (m) and 3490 (m).

Comparison of this spectrum with that obtained from reagent grade acetone vapor showed the bands at wavenumbers 580 (m), 660 (w), 1270 (m), 1300 (s), 1430 (w), 2210 (s), 2230 (s), 2350 (w), 2560 (w), 2800 (w), 3020 (m) and 3490 (m) to be attributable to irradiation products.

Decreasing the temperature at which the product gases were collected resulted in reduction of band intensities as shown in Table 1. Dashes indicate the absence of the band.  $T_c$  represents the temperature in degrees centigrade at which the product gases were collected.

$T_c$	WAVENUMBER					
	580	660	1270	1300	1430	2210
20.0	m	w	m	s	w	s
-3.0	m	-	-	m	w	m
-78.5	w	-	-	m	-	w
-195.8	w	-	-	w	-	-

$T_c$	WAVENUMBER					
	2230	2350	2560	2800	3020	3490
20.0	s	w	w	w	m	m
-3.0	m	-	-	-	w	-
-78.5	w	-	-	-	-	-
-195.8	-	-	-	-	-	-

Table 1. Infrared absorption bands for gaseous products obtained from ultraviolet irradiation of a solution of HMX dissolved in acetone.

The gaseous products obtained at 20° C from an 18 hour irradiation of HMX in the solid state yielded a spectrum showing absorption bands at wavenumbers 270 (s), 580 (m), 660 (m), 820 (s), 1280 (m), 1430 (s), 1760 (m), 2210 (m), 2230 (m) and 2350 (m). The spectrum obtained from the sample collected at -78.5° C showed that the intensity of the bands at wavenumbers 580, 2210, 2230 and 2350 had been reduced and the bands at wavenumbers 660 and 1280 had been altogether eliminated.

The infrared spectrum of the gaseous products from the solid-state irradiation of HMX under an atmosphere of helium at a pressure of 20 cm. of mercury differed from those of the solid-state irradiation of



HMX under high vacuum only in that it lacked the bands at wavenumbers 660 and 2350 and that the bands at wavenumbers 2210 and 2230 were of lesser intensity.

The nuclear magnetic resonance spectra obtained gave no evidence of proton presence in the isolated brown solid product.

The results of mass spectroscopic analysis of gaseous samples obtained from irradiation of HMX-acetone solutions are summarized in Table 2. Quantities are expressed as percentages relative to major product.

T <sub>c</sub>	MASS TO CHARGE RATIO									
	13	14	15	16	26	27	28	29	30	31
20.0	2.0	8.0	34.0	3.5	5.5	9.3	12.7	4.1	0.1	0.5
-78.5	0.5	11.0	3.4	3.0	0.9	1.5	100	1.6	1.9	0.0

T <sub>c</sub>	MASS TO CHARGE RATIO								
	32	38	39	40	41	42	43	44	58
20.0	0.1	1.2	3.8	0.9	1.9	7.5	100	4.2	24.0
-78.5	6.7	0.1	0.3	1.7	0.2	0.5	5.8	5.5	3.0

Table 2. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of a solution of HMX dissolved in acetone.

The results obtained from the irradiation of a solution of HMX dissolved in acetone-d<sub>6</sub> are shown in Table 3. Quantities obtained for each mass-to-charge ratio (m/e) are expressed as percentages relative to major products (%).

m/e	14	16	18	28	30	32	34
%	1.9	2.4	35.5	5.4	8.7	1.6	1.6
m/e	40	42	44	45	46	47	64
%	1.3	1.6	6.3	1.5	100	2.3	30.0

Table 3. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of a solution of HMX dissolved in acetone-d<sub>6</sub>.



The results obtained from analysis of vapors collected at 20° C from non-irradiated (N) and irradiated (I) reagent grade acetone are shown in Table 4. Quantities are expressed as percentages relative to major product.

m/e	14	15	16	26	27	28	29	30
N	6.8	33.3	0.5	5.5	8.9	1.9	3.8	0.2
I	12.7	57.1	2.8	8.4	13.5	31.9	7.3	3.1

m/e	38	39	40	41	42	43	44	58
N	1.3	4.0	0.8	2.1	7.5	100	2.4	25.0
I	1.2	4.1	1.1	2.2	7.5	100	3.5	25.9

Table 4. Mass to charge ratios of gaseous products obtained from ultraviolet irradiated and non-irradiated reagent grade acetone.

The results from analysis of gaseous products obtained at various temperatures from irradiation of HMX in the solid state are shown in Table 5. Quantities are expressed as percentages relative to the major product.

T <sub>c</sub>	MASS TO CHARGE RATIO							
	14	16	28	29	30	32	40	44
20.0	10.9	3.1	100	0.8	0.4	17.6	1.9	1.3
-78.5	10.6	3.2	100	0.8	0.1	18.8	2.0	0.5
-195.8	11.5	3.2	100	0.9	0.0	20.5	2.5	0.4

Table 5. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of solid-state HMX under a pressure of 0.001 Torr.

The results from analysis of gaseous products obtained at 20° C from irradiation of HMX in the solid state under an atmosphere of helium at a pressure of 20 cm. of mercury are shown in Table 6.

m/e	14	28	30	44
%	17.1	100	67.0	51.5

Table 6. Mass to charge ratios of gaseous products obtained from ultraviolet irradiation of solid-state HMX under an atmosphere of helium at a pressure of 20 cm. of mercury.

The mass loss upon irradiation of the 0.2784 grams of solid HMX exposed to the atmosphere was found to be 0.0006 grams after a period of 90 minutes and 0.0025 grams after a period of 180 minutes.

The mass loss upon irradiation of the 0.5036 gram sample for 18 hours was found to be 0.0567 grams or  $1.91 \times 10^{-3}$  moles. Using the ideal gas law the 65 cm. Hg of gaseous products evolved was found to represent  $1.99 \times 10^{-2}$  moles of gas evolved.

The melting point obtained for HMX was  $278 \pm 2^\circ$  C. The melting point obtained for the isolated water-soluble product was  $88 \pm 2^\circ$  C.

Analysis of the drop-test data showed that the non-irradiated HMX required a drop height of 35 cm. for 50% probability of detonation, whereas for the sample irradiated for 30 minutes a drop height of 78 cm. was required to obtain the same probability.

## V. DISCUSSION

The reduction of nitramine concentration with increased irradiation time as shown by the thin-layer chromatograms indicates that ultraviolet irradiation of an HMX-acetone solution results in destruction of the N-NO<sub>2</sub> chromophore. The lack of evidence for the presence of nitramines other than HMX was not considered sufficient to eliminate this possibility, due to the low [HMX] necessitated by solubility limits [31]. Destruction of the N-NO<sub>2</sub> chromophore is also shown by the ultraviolet and infrared absorption spectra.

Using the correlation charts provided by Beckman Instrument Corporation and Refs. 32, 33, 37, 38 and 39 the major products obtained at 20° C from HMX-acetone solution irradiation (Table 1) were identified. The bands at wavenumbers 660 (w) and 2350 (w) were assigned to CO<sub>2</sub>, those at 1300 (s), 2210 (s) and 2230 (s) to N<sub>2</sub>O. The band at wavenumber 3020 (m) was attributed to a mixture of CH<sub>2</sub>O and C<sub>2</sub>H<sub>4</sub>. The band expected at wavenumber 1700 for CH<sub>2</sub>O was considered to have been masked by a strong acetone band in that region. Since the boiling (sublimation for CO<sub>2</sub>) points of the identified products decrease in the order CH<sub>2</sub>O, CO<sub>2</sub>, C<sub>2</sub>H<sub>4</sub> and N<sub>2</sub>O [29], the decrease in band intensities with decreasing T<sub>c</sub> as noted in Table 1 are in agreement with these assignments.

Using the same references as above, the major gaseous products obtained at 20° C from the solid-state irradiation of HMX were identified. The bands at wavenumbers 660 (m), 2350 (m), 1280 (m), 2210 (m) and 2230 (m) again indicated the presence of CO<sub>2</sub> and N<sub>2</sub>O. The band at wavenumber 1430 (s) was attributed to C<sub>2</sub>H<sub>6</sub>. The decrease in band intensities with decreased T<sub>c</sub> was again in agreement with these assignments.

For the sample obtained from irradiation of solid-state HMX under a helium atmosphere the lack of bands at wavenumbers 660 and 2350 indicated that formation of  $\text{CO}_2$  was reduced below the limits of detectability. The lack of the  $\text{CO}_2$  bands was determined with the use of a consistent product peak as an internal reference.

The infrared spectra obtained from the isolated water-soluble solid product showed no indication of the presence of N-H or C-H bonds. This observation was in agreement with the lack of protons as indicated by the nuclear magnetic resonance spectrum. The broad band around wavenumber 3400 was attributed to  $\text{H}_2\text{O}$  absorbed by the product. The broad, ill-defined bands at wavenumbers 1380 and 1670 were not identified.

As shown in Table 2, the major products obtained at  $20^\circ\text{C}$  from irradiation of HMX-acetone solution were those having mass-to-charge ratios of 15, 28, 43 and 58. With the use of Ref. 33 these ratios were assigned as follows: 15 ( $\text{CH}_3^+$ ), 28 ( $\text{N}_2$ ,  $\text{C}_2\text{H}_4$ ), 43 ( $\text{O}=\text{C}^+-\text{CH}_3$ ), 58 (acetone). The reduction of the peaks at ratios 15, 43 and 58 and the emergence of 28 as the major peak at  $T_c$  of  $-78.5^\circ\text{C}$  was consistent with these assignments. The shifts of the peaks at ratios 15, 43 and 58 to ratios 18, 46 and 64 when acetone- $\text{d}_6$  was used as the solvent (Table 4) identified these peaks as being due to the solvent.

Again referring to Table 2 it is seen that upon removal of most of the solvent by collecting the sample at  $-78.5^\circ\text{C}$  the major peaks occurred at m/e ratios of 14, 28, 32 and 44. These peaks were assigned as follows: 14 (N), 28 ( $\text{N}_2$ ,  $\text{C}_2\text{H}_4$ ), 32 ( $\text{O}_2$ ), 44 ( $\text{N}_2\text{O}$ ,  $\text{CO}_2$ ). The



possibility of a portion of the peak at m/e ratio of 28 being due to CO was discounted due to the lack of a CO band at wavenumber 2143 in the associated infrared absorption spectrum.

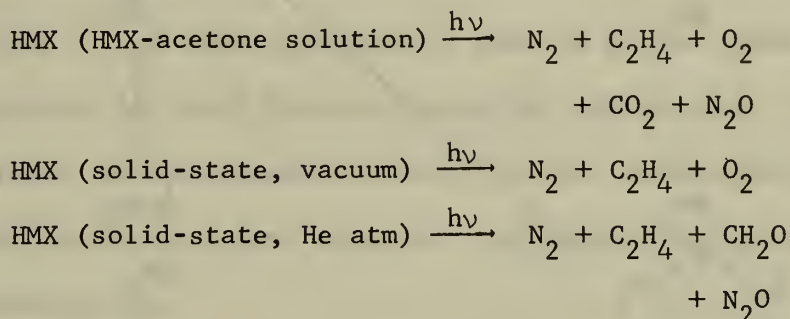
Reference 40 states that the primary products of the unquenched photochemical decomposition of acetone are  $\cdot\text{CH}_3$  and CO. Quenching of this reaction by a third body capable of absorbing excess vibrational energy from the acetyl group results in the primary products  $\text{O}=\dot{\text{C}}-\text{CH}_3$  and  $\cdot\text{CH}_3$ .

The large signal obtained at m/e ratio of 28 for the products from irradiation of pure acetone (Table 4) indicates significant formation of CO. The amount of CO obtained from irradiation of HMX-acetone solution (Table 3) is much less than that obtained from irradiation of pure acetone. This fact suggests that the unquenched mechanism for acetone photolysis is not significantly involved in the photochemical reaction of an HMX-acetone solution. The presence of the HMX may therefore account for the reduced generation of CO by quenching the acetone reaction through a third body effect. The energy thus absorbed might serve to activate the HMX, but no definite conclusions in this regard can be made without quantum yield data. The possibility of such an activation, in addition to the possibility of gas-phase reactions of acetone fragments with HMX products, necessitates caution in the interpretation of the results of HMX-acetone photolysis.

The major m/e ratios obtained from solid-state irradiation of HMX (Table 5) were assigned as follows: 14 (N), 16 (O), 28 ( $\text{N}_2$ ,  $\text{C}_2\text{H}_4$ ), 32 ( $\text{O}_2$ ). CO was considered not to be a significant product on the basis of the absence of CO bands in the associated infrared spectrum. The persistence of these peaks at temperatures down to  $-195.8^\circ\text{C}$  is

consistent with these assignments. The presence of  $\text{CO}_2$  and  $\text{N}_2\text{O}$  as noted in the infrared absorption spectrum was detected at m/e ratio of 44, but as shown in Table 5 they were minor products.

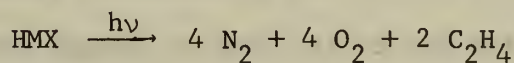
The major products obtained under differing irradiation environments can be summarized as below:



NO was considered not to be a significant product in the latter case due to the absence of NO bands in the associated infrared spectrum.

From the above it can be seen that  $N_2$  and  $C_2H_4$  are present in quantity under all irradiation conditions. The  $O_2$  produced by solid-state irradiation under a vacuum of  $10^{-3}$  Torr is replaced by  $CH_2O$  and  $N_2O$  when irradiation is carried out under a helium atmosphere of 20 cm. of mercury. The lack of significant amounts of  $CH_2O$ , the appearance of  $CO_2$  and the reappearance of  $O_2$  as major products upon irradiation of HMX-acetone solution were not considered to be reliable indications of HMX photolysis products due to the complications noted above.

The values obtained for mass loss and gas evolution upon solid-state irradiation of HMX under vacuum indicated that each mole of HMX reacted yields ten moles of gaseous products. The production of  $N_2$ ,  $O_2$  and  $C_2H_4$  is stoichiometrically consistent with this ratio as shown below:



a proposed mechanism accounting for these products is shown as Figure 2.

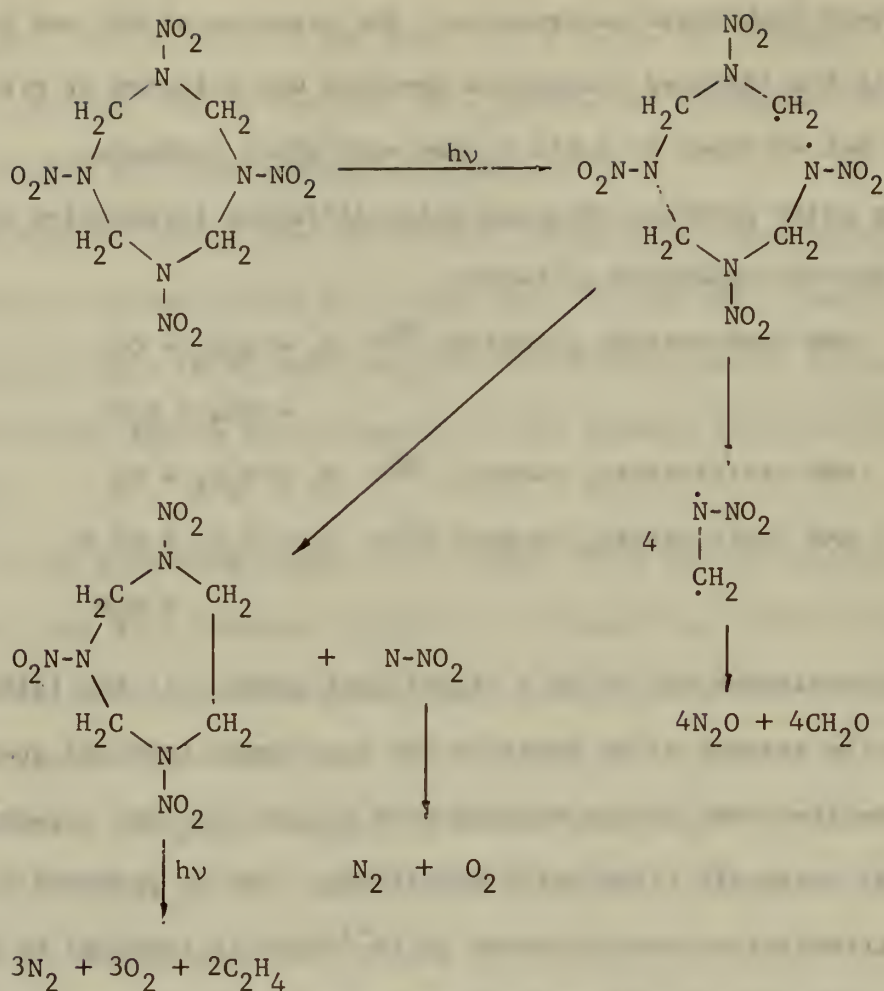


Figure 2. Proposed mechanism for photochemical decomposition of HMX.

The mechanistic pathway leading to the products  $\text{N}_2$ ,  $\text{O}_2$  and  $\text{C}_2\text{H}_4$  is supported by the data presented in Figure 1, which shows that with increased irradiation period the  $\text{N-NO}_2$  in the solid residue decreased. Since each sample analyzed was prepared from the same mass of product, this indicated that some product was formed having fewer  $\text{N-NO}_2$  chromophores per gram than the original HMX. The presence of such an intermediate product is also indicated by the reduced shock sensitivity as demonstrated by the drop-test data. The intermediate species would be expected to be less sensitive due to the reduced oxygen balance.

The mechanistic pathway leading to the products  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  is the same as the mechanism proposed by Maycock, et. al. [25].

The experimental results indicate that the predominant mechanistic pathway will be in some manner determined by the pressure under which the irradiation is conducted. It should also be recognized that the production of  $\text{N}_2\text{O}$  and  $\text{CH}_2\text{O}$  might in part be due to thermal decomposition brought about by local heating within the HMX crystal. More definite conclusions in these regards require further investigation utilizing equipment capable of more effective temperature and pressure control and determination.



## VI. BIBLIOGRAPHY

1. Bachman, W. E., and Sheehan, J. C., "A New Method of Preparing the High Explosive RDX," Journal of the American Chemical Society, v. 71, p. 1842-1845, May 1949.
2. McCrone, W. C., "Cyclotetramethylene Tetranitramine (HMX)," Analytical Chemistry, v. 22, no. 9, p. 1225-1226, September, 1950.
3. Eiland, P. F. and Pepinsky, R., "The Crystal Structure of Cyclotetramethylenetetranitramine," Zeitschrift Fur Kristallographie, v. 106, p. 273-298, August 1955.
4. Pepinsky, R., "New X-Ray and Neutron Studies of Hydrogen Bonding," Reviews of Modern Physics, v. 30, p. 100, January 1958.
5. Huber, H., Meyers, J. L., and Wright, G. F., "The Crystalline Form of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane (HMX)," Canadian Journal of Chemistry, v. 40, p. 2278-2299, December 1962.
6. Fischer, H., "The Preparation of Octogen (Cyclotetramethylene-tetranitramine)," Chemische Berichte, v. 82, p. 192-193, April 1949.
7. Chute, W. J., Downing, D. C., McKay, A. F., Meyers, G. S., and Wright, G. F., "The Nitrolysis of Hexamethylenetetramine. I. The Significance of 1,5-Endomethylene-3,7-Dinitro-1,3,5,7-Tetrazacyclooctane," Canadian Journal of Research, v. 27B, p. 218-237, November 1949.
8. Aristoff, E., Graham, J. A., Meen, R. H., Myers, G. S., and Wright, G. F., "Recombination of Fragments During Hexamethylenetetramine Nitrolysis in Acetic Anhydride," Canadian Journal of Research, v. 27B, p. 520-544, December 1949.
9. McKay, A. F., Richmonds, H. H., and Wright, G. F., "Nitrolysis of Hexamethylenetetramine. II. Nitrolysis of 1,5-Endomethylene-3,7,-Dinitro-1,3,5,7-Tetrazocyclooctane (DPT)," Canadian Journal of Research, v. 27B, p. 462-468, December 1949.
10. Bachman, W. E., Horton, W. J., Jenner, E. L., MacNaughton, N. W., and Scott, L. B., "Cyclic and Linear Nitramines Formed by Nitrolysis of Hexamine," Journal of the American Chemical Society, v. 75, p. 2769-2773, June 1951.
11. Epstein, S. and Winkler, C. A., "RDX and HMX Production in the Bachmann Reaction," Canadian Journal of Chemistry, v. 30, p. 734-742, October 1952.

12. Wright, G. F. and Chute, W. J., Nitramines, U.S. Patent 2,678,927, 18 May 1954.
13. Thatcher, D. N., Separation of Cyclotetramethylenetetranitramine from Cyclotrimethylenetrinitramine, U.S. Patent 2,900,381, 18 August 1959.
14. Silberman, L. B., Preparation of HMX by Using Boron Trifluoride, U.S. Patent 2,941,994, 21 June 1960.
15. Picard, J. P., Homocyclonite, U.S. Patent 2,983,725, 9 May 1961.
16. Bachmann, W. E. and Deno, N. C., "The Nitrosation of Hexamethylenetetramine and Related Compounds," Journal of the American Chemical Society, v. 73, p. 2777-2779, June 1951.
17. Bachmann, W. E. and Jenner, E. L., "1-Acetoxymethyl-3,5,7-Trinitro-1,3,5,7-Tetrazocyclooctane and its Reactions. Significance in the Nitrolysis of Hexamethylenetetramine and Related Compounds," Journal of the American Chemical Society, v. 73, p. 2773-2775, June 1951.
18. Werbin, A., "The Infrared Spectra of HMX and RDX," U.S. Atomic Energy Commission UCRL-5078, 8 pages, 1957.
19. Jones, R. N. and Thern, G. D., "The Ultraviolet Absorption Spectra of Aliphatic Nitramines, Nitrosamines, and Nitrates," Canadian Journal of Research, v. 27B, p. 828-860, December 1949.
20. Schroeder, W. A., Wilcox, P. E., Trueblood, K. N., and Dekker, A. O., "Ultraviolet and Visible Absorption Spectra in Ethyl Alcohol. Data for Nitric Esters, Nitramines, Nitroalkylbenzenes and Derivatives of Phenol, Aniline, Urea, Carbamic Acid, Diphenylamine, Carbazole, and Triphenylamine," Analytical Chemistry, v. 23, p. 1740-1747, October 1951.
21. Robertson, A. J. B., "Thermal Decomposition of Explosives. II. Cyclotrimethylenetetranitramine (Cyclonite) and Cyclotetramethylenetetranitramine," Transactions of the Faraday Society, v. 45, p. 85-93, January 1949.
22. Maksinov, Yu. Ya. "Thermal Decomposition of Hexogen and Octogen," Transcripts of the Moscow Chemical and Technological Institute, v. 53, p. 73-84, 1967.
23. Suryanarayana, B., Graybush, R. J., and Autera, J. R., "Thermal Degradation of Secondary Nitramines: A Nitrogen-15 Tracer Study of HMX (1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclooctane)," Chemistry and Industry, v. 52, p. 2177-2178, 30 December 1967.
24. Suryanarayana, B., Autera, J. R., and Graybush, R. J., "Effect of Ultraviolet Irradiation of Phase Transformations in Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine Polymorphs," Molecular Crystals, v. 2(4), p. 373-377, 1967.

25. Maycock, J. N., Verneker, V. R. Pai, and Lochte, W., "Physico-Chemical Properties of 1,3,5,7-Tetranitro-1,3,5,7-Tetrazacyclo-octane (HMX). II. Spectra and Ultraviolet Radiation Damage Phenomena," Physica Status Solidi, v. 35, no. 2, p. 849-860, October 1969.
26. Kaufman, J. V. R., "The Effect of Nuclear Radiation of Explosives," Proceedings of the Royal Society, v. 246, p. 219-225, 29 July 1958.
27. Urizar, M. J., Loughran, E. D., and Smith, L. C., "Nuclear Radiation Effects on Organic Explosives," Explosivstoffe, v. 10, no. 3, p. 55-64, 1962.
28. Mallay, J. F. and Prask, H. J., "Inadequacy of Thermal Initiation Theory in Interpreting the Results of Fission-Fragment Irradiation of Explosives at Elevated Temperatures," Nature, v. 203, p. 473-476, 1 August 1964.
29. Lange's Handbook of Chemistry, 10th ed., McGraw-Hill, 1967.
30. NAVWEPS Report 8575, Technical Report 151, Separation of RDX and HMX by Thin-Layer Chromatography, by M. E. Fauth and G. W. Roecker, 21 pages, 4 June 1964.
31. Harthorn, J. G. L., "Thin-Layer Chromatography of Some Nitramine Explosives," Acta Chemica Scandinavia, v. 15, p. 1401-1402, 1961.
32. Willard, H. H., Merritt, L. L., Jr., and Dean, J. A., Fundamental Methods of Analysis, 4th ed., ch. 4-5, Van Nostrand, 1965.
33. Silverstein, R. M. and Bassler, G. C., Spectrometric Identification of Organic Compounds, 2nd ed., p. 115, Wiley, 1968.
34. United States Naval Postgraduate School Technical Report no. 16, The Effect of Explosive Mixtures Upon Impact Sensitivity, by J. E. Sinclair, p. 4-17, March 1957.
35. Nagakura, S., "Intramolecular Charge Transfer Spectra Observed with Some Compounds Containing the Nitro or Carbonyl Group," The Journal of Chemical Physics, v. 23, no. 8, p. 1441-1445, August 1955.
36. Stals, J., Barraclough, C. G., and Buchanan, A. S., "Molecular Orbital Interpretation of the Ultra-Violet Absorption Spectra of Unconjugated Aliphatic Nitramines," Transaction of the Faraday Society, v. 65, p. 904-914, April 1969.
37. Verdier, P. H. and Wilson, E. B., Jr., "Force Constant Calculations in Linear Triatomic Molecules from Infrared and Microwave Data," Journal of Chemical Physics, v. 30, no. 5, p. 1372-1373, May 1959.
38. Herzburg, G., Molecular Spectra and Molecular Structure. I. Spectra of Diatomic Molecules, 2nd ed., p. 30-53, Van Nostrand, 1950.



39. Herzburg, G., Molecular Spectra and Molecular Structure. III. Electronic Spectra and Electronic Structure of Polyatomic Molecules, p. 488-513, Van Nostrand, 1966.
40. Calvert, J. G. and Pitts, J. N., Jr., Photochemistry, p. 366-462, Wiley, 1966.

# INITIAL DISTRIBUTION LIST

	No. Copies
1. Defense Documentation Center Cameron Station Alexandria, Virginia 22314	20
2. Library, Code 0212 Naval Postgraduate School Monterey, California 93940	2
3. Chief of Naval Research Department of the Navy Washington, D.C. 20360	1
4. Associate Professor C. F. Rowell, Code 5413 Department of Material Science and Chemistry Naval Postgraduate School Monterey, California 93940	2
5. LCDR J. B. Torbit, USN 15030 Colson Avenue Dearborn, Michigan 48126	1



## DOCUMENT CONTROL DATA - R &amp; D

(Security classification of title, body of abstract and indexing annotation must be entered when the overall report is classified)

1. ORIGINATING ACTIVITY (Corporate author)

Naval Postgraduate School  
Monterey, California 93940

2a. REPORT SECURITY CLASSIFICATION

Unclassified

2b. GROUP

3. REPORT TITLE

THE PHOTOCHEMICAL DECOMPOSITION OF 1,3,5,7-TETRANITRO-1,3,5,7-TETRACYCLOOCTANE (HMX)

4. DESCRIPTIVE NOTES (Type of report and, inclusive dates)

Master's Thesis; April 1970

5. AUTHOR(S) (First name, middle initial, last name)

LCDR Jerry Bert Torbit, United States Navy

6. REPORT DATE

April 1970

7a. TOTAL NO. OF PAGES

41

7b. NO. OF REFS

40

8a. CONTRACT OR GRANT NO.

b. PROJECT NO.

c.

d.

9a. ORIGINATOR'S REPORT NUMBER(S)

9b. OTHER REPORT NO(S) (Any other numbers that may be assigned  
this report)

10. DISTRIBUTION STATEMENT

This document has been approved for public release and sale; its distribution  
is unlimited.

11. SUPPLEMENTARY NOTES

12. SPONSORING MILITARY ACTIVITY

Naval Postgraduate School  
Monterey, California 93940

13. ABSTRACT

This investigation was concerned with the photochemical decomposition of 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (HMX). Products from ultraviolet irradiation of both solid-state HMX and HMX-acetone solutions were obtained and identified.

On the basis of observed product variability with irradiation environment a new mechanism for the photochemical decomposition of HMX was postulated.

### KEY WORDS

LINK C

WT

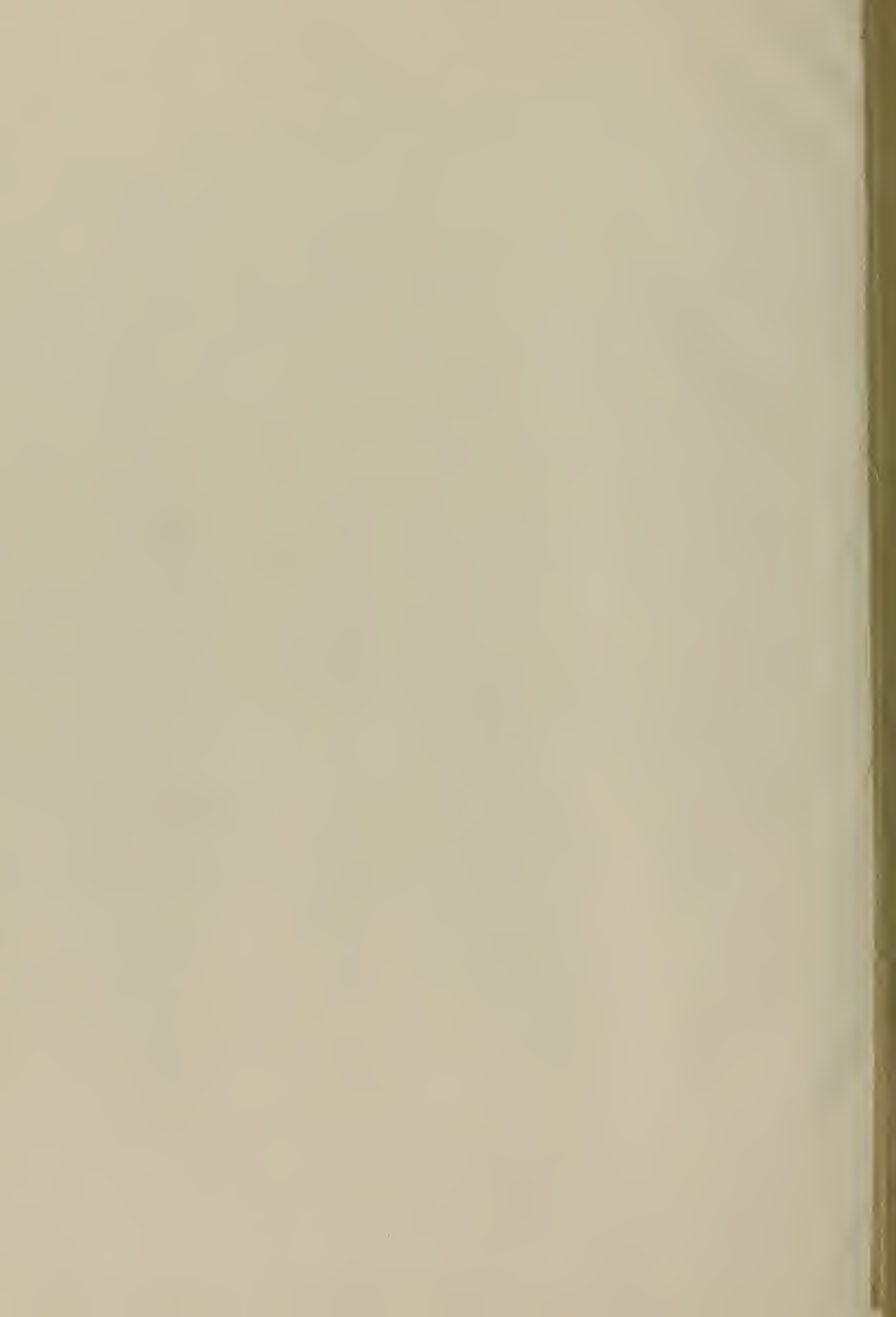
## Photochemical Decomposition











10 OCT 72

21991

Thesis

120100

T753

Torbit

c.1

The photochemical  
decomposition of 1,3,  
5,7-tetranitro-1,3,5,  
7-tetrazacyclooctane

10 OCT (HMX)

21991

Thesis

120100

T753

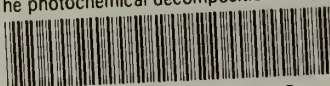
Torbit

c.1

The photochemical  
decomposition of 1,3,  
5,7-tetranitro-1,3,5,  
7-tetrazacyclooctane  
(HMX)

thesT753

The photochemical decomposition of 1, 3,



3 2768 002 03595 8

DUDLEY KNOX LIBRARY